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An investigation on the fatigue based delamination of woven carbon-epoxy composite laminates reinforced with polyamide nanofibers

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Abstract

Delamination is the most frequent failure mode in laminated composite materials and it may cause catastrophic failure in critical engineering structures. One of the ways to prevent this failure is to toughen the crack against initiation and propagation. There is lack of studies in literature for toughening the delamination using nanofibers, especially in the case of fatigue behavior. Therefore, the present work aims to investigate effect of interleaved nanofiber mat on fatigue interlaminar properties of mode I delamination in carbon-epoxy composite laminates. To reach this aim, the electrospun polyamide nanofiber fabrics were put in the mid-plane of woven carbon/epoxy laminates. Then the fatigue Double Cantilever Beam (DCB) tests were performed on both virgin and nanomodified specimens, based on ASTM D6115. The experimental results show that the interlaminar fracture toughness and delamination onset fatigue life of the specimens can be substantially improved by addition of the Polyamide nanofiber interlayer. As a matter of fact, there is negligible increase in the thickness of the specimens, less than 1%, but there is noticeable out-plane mechanical properties increase of the modified specimens. The increases in the delamination toughness are up to 150%, at the static tests, and around 100% at the high cycle fatigue loading conditions. Crack paths were investigated by micrograph analysis and different behaviors in the virgin and nano-modified ones were observed and related to the different mechanical results.

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Keywords: FRP; Nanofiber; Interleaving; Interlaminar fracture toughness; Fatigue delamination; Mode I

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1. Introduction

In the few last decades there has been a growing interest in the use of composite laminates in structural applications ranging from aircraft structures to marine and automotive applications. In most of them thermoset polymers such as epoxy has been applied as matrix, but their inherent brittleness restricts their application, because the laminates can be delaminated easily during their service even with a very low energy of impact [1-3]. Many methods have been introduced to resolve or at least decrease this problem [4-5], but each one can make another problem for the laminates. For example, the tensile strength can be decreased by stitching the laminates [6].

Recently, a novel method has been introduced in which nanofibrous mat manufactured by thermoplastic polymers were interleaved between composite layers [7]. So far, different polymers such as Nylon 6,6 [8-10], Polysulfone (PSF) [11], polyvinylidene fluoride (PVDF) [12], PCL [8] and etc have been used for increasing the delamination resistance of composite laminates.

Some studies have been conducted regarding the effect of nanofibers on mode-I and mode-II fracture toughness. Saghafi et al. [8] used Nylon 6,6, PCL and their mixture to increase the fracture toughness. Their results showed that while Nylon 6,6 are only useful for mode II loading and PCL effect is almost the same in mode I and mode II, the mixed nanofibers could use the efficiency of both individual nanofibers in modes I and II. In another study [12], they used PVDF nanofibers for interleaving composite laminates. Mode-I fracture tests were conducted and the outcomes proved 43% increase of mode-I energy release rate (G_I), which was in contrast with the results of two other studies [13-14]. According to the results presented by Li et al. [11], PSF is a very suitable choice for increasing fracture toughness of epoxy-based composite as increased mode-I fracture toughness about 280%.

There are also some studies regarding the effect of nanofibers on impact response of composite laminates. Palazzetti et al. [15] and Akangah et al. [16] used Nylon 6,6 nanofibers for decreasing delaminated area of composite materials under low-velocity impact. The dynamic response of interleaved laminates was also investigated by [15]. They showed that the undamaged nanomodified laminates are less stiff but significantly more damped respect to virgin ones.

Fatigue behavior of nanofiber-interleaved laminates is another important issue, but very limited researches have been published [17-19]. In all these studies, carbon nanofibers (CNF) were applied to consider its effect on mode-I fatigue response of modified laminates. Zhou et al. [17-18] conducted a comprehensive investigation: tensile, fatigue, uniaxial compression, open-hole compression, short beam shear, and flexure tests were performed. They mixed carbon nanofibers with the epoxy and then produced their laminates using vacuum assisted resin transfer molding (VARTM) method. Some mechanical properties such as tensile and flexural strength increased moderately, 11 and 22% respectively, but others like fatigue strength improved significantly. Arai et al. [19] put CNF between carbon/epoxy layers and conducted mode-I fracture and fatigue tests. The test results show that the number of cycles to failure becomes 1.5 times greater than reference laminates.

As mentioned before, also the use of Nylon nanofibers is a good choice for increasing fracture toughness of composite laminates. However there is still a lack of studies in literature regarding the fatigue behavior of Nylon nanofiber-interleaved laminates. At the present, only Shivakumar et al. [29] studied the effect of Nylon 66 on the fatigue delamination toughness and its investigation was focused on UD laminates. Therefore, in this work was investigated the fatigue behavior at delamination of woven laminates interleaved with Nylon 66 nanofibers. Mode I quasi-static and fatigue delamination grow onset test were performed and the crack path was investigated by micrograph analysis in order to better understand the toughening mechanism.

2. Materials and Methods

2.1. Materials

Plain Weave (PW) 220gsm carbon-epoxy prepreg (GG204P-IMP503Z), supplied by Impregnatex Composite Srl (Milan, Italy), was chosen as base material to improve its interlaminar fracture toughness by nanofiber interleaving. Its matrix is based on diglycidyl ether of bisphenol A prepolymer, has a glass transition temperature *Tg* of 120 °C and is characterized by good mechanical properties and toughness.

Nylon 66 Zytel E53NC010, provided by DuPont, were used for producing nanofibers. It has extremely high elongation at brake and toughness (compared to the epoxy matrix), and a melting temperature of 260 °C (therefore the nanofibers don't melt during the prepreg curing process).

2.2. Electrospinnig process

Nylon 66 nanofibers were produced by means of electrospinning technique [9]. The polymer was dissolved at a concentration of 20%, in a solution composed by Formic Acid and Chloroform Cromasolv® (50:50 v/v), purchased from Sigma Aldrich. The nanofibrous mats were fabricated using a Spinbow® electrospinng machine (Fig. 1a) equipped with a four- needle firing system and a rotating drum collector covered with polythene paper, in which the fibers are collected and safely removed, once the process is finished. The process was carried out under the following conditions: 24 kV voltage, 15 cm needle tip – collector distance, 0.3 mL/h flow rate per nozzle, 20-23 °C temperature with 40-45 % of relative humidity (RH), 0.2 m/s tangential speed of the drum and 450 min process duration. The scanning electron microscope (SEM) image of the electropsun non-woven mat, so obtained, is shown in (Fig. 1 b). The nanofibers were random aligned and their diameter ranged from 400 to 650 nm. The electrospun mat was 40 μm thick, with an areal density of 18 g/m^2. The mat was kept in oven at 40 °C overnight, before integrating it into the laminate, in order to remove residual solvent and the moisture absorbed by the Nylon.

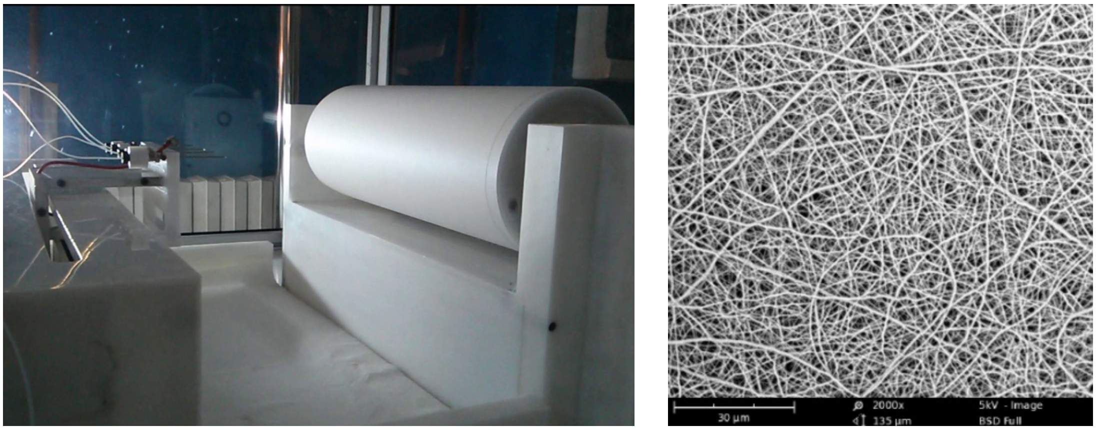

Fig. 1. (a) Electrospinning machine; (b) Morphology of the Nylon 66 electrospun non-woven mat.

2.3. Lamination process

Two panels, one for the unmodified laminate (*Virgin*) and another one for the nano-interleaved (*Ny*), with dimensions of 300x170 mm^2, were manufactured by stacking 14 plies of prepreg. A PTFE film (30 μm thick) was inserted in the mid-thickness during the lay-up, in order to create the artificial crack. In the case of the nano-interleaved laminate, the nanofibers were incorporated in the mid plane, using a technique similar to the "Action Transfers" one: the electrospun mat, still with the polythene sheet, was applied to the prepreg, by rolling it softly until it has been transferred to the sticky resin; then the polythene sheet was peeled off and the another prepreg ply was stacked on it. In this way the electrospun mat was completely transferred to the prepreg without delaminate it.

Then, both panels were placed on a glass (to ensure the planarity) and inserted in the vacuum bag using the same industrial technique used for vacuum bag molding. The specimens were kept first under vacuum (850 mbar) for 24 hours at room temperature. Later, they were cured in autoclave, under a pressure of 6 bar, for 2 hours at 60 °C and then for 1 hour at 130°C. Note that the curing cycle is specifically optimized in order to ensure the perfect penetration of the resin into the nanofibrous mat, before the hardening occurs.

2.4. Test: Mode I Quasi-static and Fatigue

Mode I interlaminar fracture toughness of the laminates was evaluated by the double cantilever beam (DCB) test. 12 specimens were extracted from each panel (discarding the edges). Each specimen was 130 mm long and 20 mm wide and had an initial delamination length (a_0) around 45 mm. The measured thickness of the laminates was 3.5±0.1 mm and no significant difference between the virgin laminates and the interleaved ones was appreciated. The tests were carried out using a servo-hydraulic press (Instron 8033) equipped with a 250 N load cell. The load was introduced to the specimens by loading blocks (Fig. 2).

The quasi-static test was performed on at least 3 specimens for each type of laminate, in displacement control at a constant crosshead rate of 3mm/min. During the test, the load-displacement curve was recorded and the crack propagation was visually determined by the means of an optical microscope. The Mode I energy release rate G_I was determined according to the Modify Beam Theory (MBT), as suggested by the protocol ASTM D5528 [21]:

$$G_I = \frac{3P\delta}{2b\left(a+|\Delta|\right)} \tag{1}$$

where P is the load, δ is the displacement, b the width of the specimen, a the delamination length and Δ is the delamination length correction parameter, to consider the beam rotation at the delamination front. The initial fracture toughness G_{IC} was evaluated according to the 5% compliance deviation or maximum load point of the loading-displacement curve [21]. The fracture toughness resistance (at propagation stage) G_{IR} was evaluated on the R-curve as average value, when after the initiation it becomes nearly constant.

The Mode I fatigue delamination growth onset test was carried out, in accordance with the ASTM D6115 [22] standard. The test apparatus was the same of the quasi-static one, as the specimen's dimensions and the panels from which they were extracted (the same batch). All fatigue tests were performed in displacement control, at a frequency of 1 Hz with a fixed loading ratio: $R= P_{min-n} /P_{max-n} =\delta_{min-n} /\delta_{max-n} =0.3$. At each *n-cycle*, the maximum (minimum) value of the displacement and load, P_{max-n} and δ_{max-n} (P_{min-n} and δ_{min-n}) were recorded. Specimens were tested at different values of G_{Imax}. Where G_{Imax} is the maximum mode I energy release, calculated by means of the modified beam equation (1), where: P and δ are equal to P_{max-1} and δ_{max-1} evaluated at the first cycle, a is the initial delamination length (a_0) and Δ is extrapolated from the quasi-static test. The fatigue test was stopped when the specimens compliance, $C=(\delta_{max\ n}-\delta_{min\ n})/(P_{max\ n}-P_{min\ n})$, has increased by 5% and the related fatigue delamination onset life, $N_{5\%}$ (equal to the cycles number achieved during the test) was recorded. The same procedure was repeated for each laminate type on at least 6 specimen at different value of G_{Imax}, keeping constant the loading ratio $R=0.3=cost$. The results were summarized in a diagram G_{Imax}-$N_{5\%}$ showing the relationship between the cyclic strain energy release rate and the number of cycles to the onset of the delamination growth.

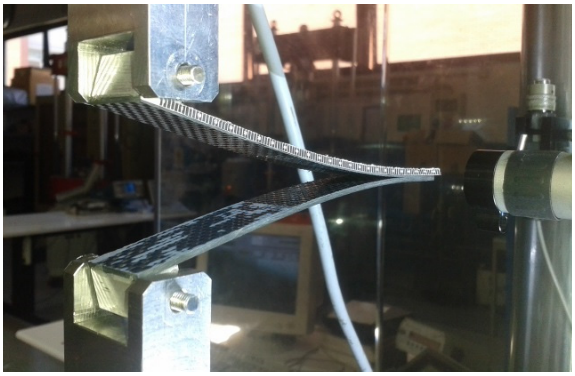

Fig. 2 DCB test setup.

3. Results

3.1. Mode I Quasi-static Fracture Toughness:

Results of mode-I fracture quasi-static tests are reported in Fig. 3 and the most relevant values are summarized in Table 1. In the load-displacement diagram of Fig. 3a, the nano-modified laminate shows the same trend of the corresponding virgin ones until the first force drop happens. However the presences of the nanofibers clearly postpone the crack initiation and increase the maximum force of 41%. Therefore, the increment provided by the nanofibers on the fracture toughness at the delamination initiation (G_{IC}) is higher (+137%).

After the first force drop, the delamination propagates in a discontinuous way and the load-displacement curves appear jagged. This behavior is strictly linked to the in-homogeneity of the interlaminar region in woven laminates. The crack, during its propagation, meets alternately zones with different toughness, due to the presence of resin pockets and the fabric texture [21]. Therefore, on the R-curve (Fig. 3b), the measured fracture toughness values appear scattered. However, unlike of what happens in the unidirectional laminates, the crack is obliged to stay in the mid-interlaminar region by the woven architecture, leading to a relatively flat R-curve (no fiber bridging). For the same reason, in the woven interleaved laminates, the crack is obliged to propagate through the reinforcement. Therefore, the presence of the nanofibers affects the fracture toughness at propagation stage, in the same way as at the initiation stage (G_R=+124%). While Shivakumar [20] noticed a decrease of the toughening effect at propagation stage (G_{IC}*=150%* vs G_R=+30%) of Nylon 66 nanofibers, interleaved in unidirectional laminates.

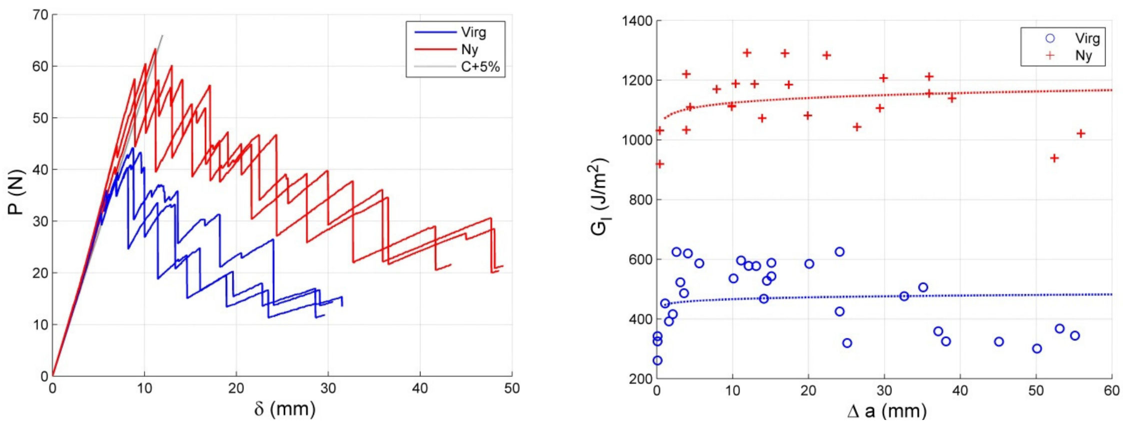

Fig. 3 (a) load-displacement curves for reference (Virg) and nano-interleaved (Ny) DCB specimens; (b) mode I interlaminar fracture toughness as a function of the delamination propagation length ($\Delta a=a-a_0$) for Virg. and Ny specimens.

Nevertheless, this behavior of woven laminates, Virgin and nano-interleaved, have to be deeply investigated and for this reason the micrographic analyses have been performed. In the initiation stage, the crack, in Virgin and nano-interleaved laminates, starts from the tip of the Teflon sheet, positioned in the mid-interlayer and it propagates through it (Fig. 4 a and c). At propagation stage, the crack tries to divert from the nano-interlayer and propagate through the adjacent not toughened carbon layer (Fig. 4 d). But the texture of the woven fabric stops the propagation of the crack inside the carbon layer, and forces it to come back in the nano-modified interlayer. For this reason, the toughening effect of the nanofibrous interleaved in woven laminate is kept also at propagation stage.

Table 1 Fracture parameters obtained for mode-I fracture tests.

	Virgin	Ny	Increase (%)
FMAX (N)	42.6 ± 2.0	60.5 ± 2.9	+41 ± 9
G_{Ic} (Initiation) (J/m^2)	420 ±30	994 ± 65	+137 ± 20
G_R (Propagation) (J/m^2)	524 ± 85	1176 ± 87	+124 ± 31

3.2. Mode I Fatigue Life

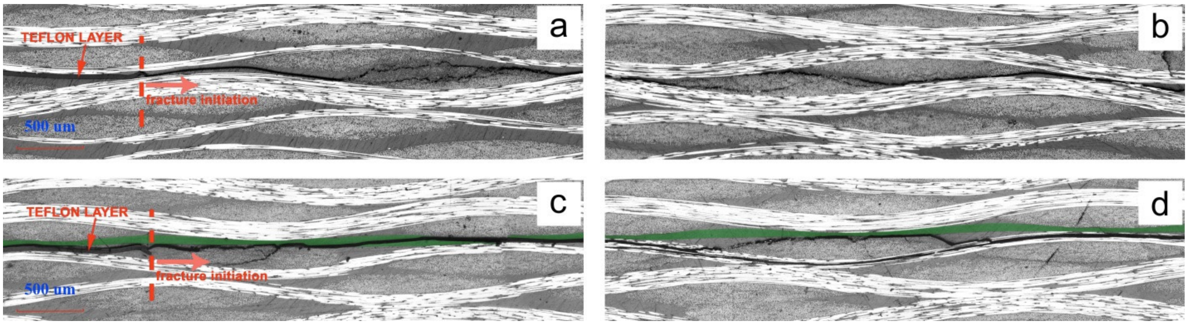

Fig. 4 Micrograph analysis of the crack path for virgin (a,b) and nano-modified (c,d) laminates at initiation and propagation. The Nylon 66 electrospun non-woven mat is highlighted in green.

The fatigue test results are plotted, as points, in the diagram maximum energy release rate G_{Imax} versus delamination onset life $N_{5\%}$, of Fig. 5. Usually, the stress-fatigue life relationship is described by a power law equation. A similar law, suggested by O'Brien in [23], was found to fit very well with the experimental data of the present work:

$$G_{\mathrm{Im}ax} = G_{IC} * N^{-m} \tag{2}$$

where G_{IC} is the fracture toughness at initiation, obtained for the quasi-static test. However, the equation expressed in this form doesn't allow an easy evaluation of the statistic confidence of the model so estimated. Therefore the Eq. 2 was linearized, by expressing it in logarithmic form:

$$\log N = A + B * \log G_{\mathrm{Im}ax} \qquad \text{or} \qquad Y = A + B * X \qquad \text{with} \qquad Y = \log N \qquad X = \log G_{\mathrm{Im}ax} \tag{3}$$

And the experimental data were plotted in a log-log diagram. The curve of Eq. 3 was extrapolated by means of the maximum Likelihood method and the confidence bands (at 95% of probability) were computed following the procedure described in ASTM D738 [24]. Then the model, with its confidence bands, was transformed back into the original form of Eq. (2) and plotted in the graph of Fig. 3.

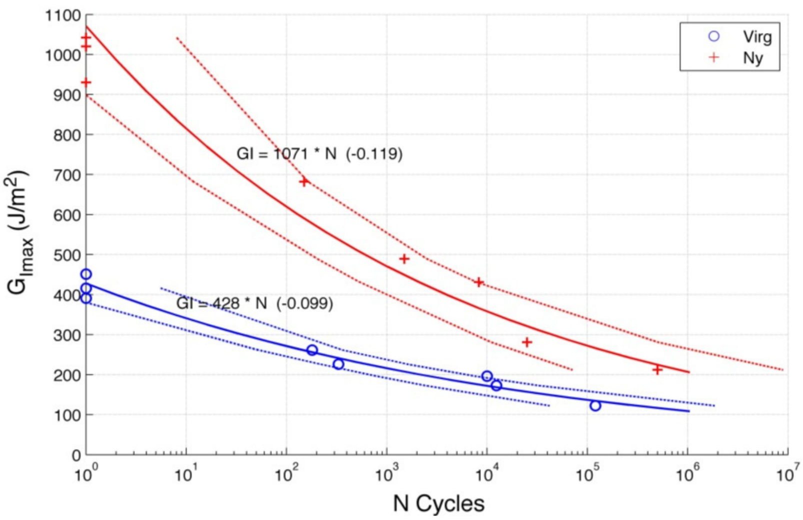

Fig. 5 DCB Fatigue diagram (GImax- N5%) at a constant load ratio R=0.3, for virgin and nano-interleaved laminates.

It's graphically clear that the model fits very well to the trend of the experimental results, however the width of the confidence bands is large because of the high scatter of the experimental data, typical of fracture tests conducted on composite material. The fatigue life equations extrapolated for the virgin and the interleaved laminates, are $G_{Imax}= 428*N^{-0.099}$ and $G_{Imax}= 1071*N^{-0.199}$, respectively. The fatigue curve of the nano-interleaved laminate begins (at $N=0$) from an energy release rate ($G_{Imax}= G_{IC}$) 2.5 times higher than the virgin one, but then it decrease faster (*m* coefficient of Eq. 2). However, it is clear that the presence of the nanofibers enhance the delamination fatigue onset life. The threshold energy release rate (estimated for $N=10^6$) of the nano-interleaved laminate is 90% higher than the virgin laminate ($G_{th\text{-}Virg}$*=109 J/m^2 vs* $G_{th\text{-}Ny}$*=207 J/m^2)*.
A micrographic analysis was performed in order to better understand the toughening mechanism of the Nylon nanofibers (Fig. 6). For both laminates, crack starts from the tip of the Teflon sheet, positioned in the mid-interlayer. Then under the cyclic loading, the crack propagates and tries to divert from the interlayer, but it's forced to come back in the interlayer by the woven architecture of the adjacent layers. In the case of the interleaved laminate, the crack is forced to propagate between the reinforced interlayer and the adjacent woven layer and this slows its propagation.

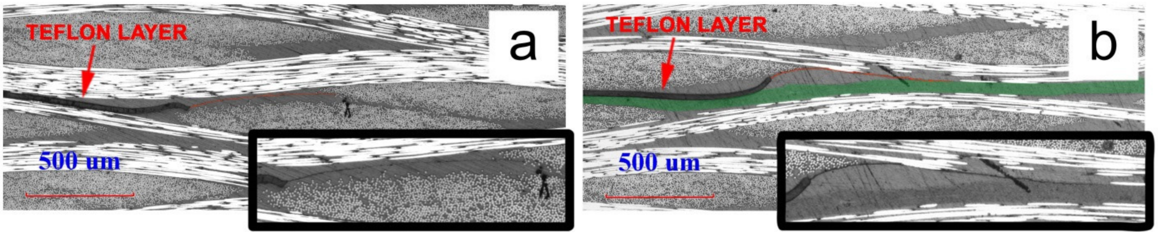

Fig. 6. Micrograph analysis of the fatigue onset delamination for: (a) Virgin and (b) nano-interleaved laminates.

4. Conclusion

The Mode I fracture toughness of woven laminates interleaved with Nylon 66 nanofibers was investigated at fatigue and quasi-static load. The results shows that the woven laminates are more suitable then UD laminates for nano-interleaving because of the fabric texture that oblige the crack to propagate through the nano-reinforced interlayer. For this reason during the quasi-static test, the toughening effect of the nanofibers was kept over 130% during the whole propagation of the crack. The hypothesized toughening mechanism was confirmed by the micrograph analysis of the crack path. Also at fatigue, the presence of the nanofibers enhance the fracture toughness at the onset of the delamination and the threshold energy release rate of the nano-interleaved laminate is 90% higher than the virgin one.

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